

## Supplemental Material for Salawitch *et al.*, Near IR Photolysis of HO<sub>2</sub>NO<sub>2</sub> Manuscript 2002GL015006

### Observations and Model Inputs

MkIV measurements of the volume mixing ratio (vmr) of HO<sub>2</sub>NO<sub>2</sub> at 35°N, sunset on Sept. 25, 1993 are given in Table 1. Measurements of HO<sub>2</sub>NO<sub>2</sub> made between ~65 and 70°N, sunrise on May 8, 1997 are listed in Table 2. The uncertainties given in the tables are 1σ estimates of the measurement precision. Uncertainty in the HO<sub>2</sub>NO<sub>2</sub> line strengths is estimated to be 20% [May and Friedl, 1993]; this is the dominant contribution to the systematic error of the HO<sub>2</sub>NO<sub>2</sub> measurement.

Model inputs for the simulations are given in Tables 3 and 4. The albedos were obtained from Total Ozone Mapping Spectrometer reflectivity data (raw data at <ftp://jwocky.gsfc.nasa.gov>) for the time and place of observation. Profiles of sulfate aerosol surface area ("Surf. Area") were obtained from monthly, zonal mean profiles measured by SAGE II [Thomason *et al.*, 1997 updated via private communication]. The profile of Br<sub>y</sub> is based on the Wamsley *et al.* [1998] relation with N<sub>2</sub>O, using MkIV measurements of N<sub>2</sub>O. All other model inputs given in Tables 3 and 4 are based on direct MkIV measurements [see Sen *et al.*, 1998 and Osterman *et al.*, 1999 for details]. Finally, we note the latitude of the MkIV tangent point varied considerably during sunrise on May 8, 1997. The simulations shown here were obtained using different latitudes for each altitude, as indicated in Table 4.

### Additional Model – Measurement Comparisons

A few additional comparisons of calculated and observed species are given here to support the conclusions of the paper. Figure 6 shows calculated HO<sub>2</sub>NO<sub>2</sub> loss frequencies (averaged over 24 hours) due to photolysis in the UV, photolysis in the near IR, and reaction with OH (results for reaction with OH are shown for the *JPL00* and *Near IR* model runs, since calculated concentrations of OH vary considerably depending on kinetic parameters). The longer days at high-latitude during spring, coupled with lower abundances of OH and lower rates of UV photolysis (due to higher slant column abundances of O<sub>3</sub>), result in near IR photolysis having a much more pronounced effect on total loss of HO<sub>2</sub>NO<sub>2</sub> for the May 1997 simulation than for the Sept 1993 model run.

Figure 7 shows that observed profiles of NO<sub>2</sub> are simulated accurately for both mid-latitudes and high-latitude spring. Revisions to the rate of OH+NO<sub>2</sub>+M in the *JPL00* compendium resolve the discrepancies discussed by Sen *et al.* [1998] and Osterman *et al.* [1999]. Most importantly, the accurate simulations of observed NO<sub>2</sub> demonstrate that uncertainties in NO<sub>x</sub> photochemistry can not explain the factor of 4 overestimate of HO<sub>2</sub>NO<sub>2</sub> at high-latitude springtime by the *JPL00* model run.

The comparison of measured OH and the four model simulations shown in Figure 8 looks similar to the HO<sub>2</sub> comparisons shown in our paper. This figure is included here to illustrate that neither the *JPL00* nor the *Model B* simulation matches the observed shape of OH versus solar zenith angle. Thus, the discrepancy discussed in the paper is for HO<sub>x</sub> (OH+HO<sub>2</sub>) and can not be accounted for by errors in the simulation of the OH to HO<sub>2</sub> ratio.

The comparisons of modeled and measured HO<sub>2</sub> shown in Figure 9 are provided to support the statement in our paper that BrONO<sub>2</sub> hydrolysis, in the absence of near IR

photolysis of  $\text{HO}_2\text{NO}_2$ , can not account for the observed shape of  $\text{HO}_2$  vs SZA near evening twilight. The model shown by the solid green curve in Figure 9 assumes a reaction probability of 0.8 for  $\text{BrONO}_2$  hydrolysis (considerably faster than expected for these conditions [D. Hanson, submitted manuscript, 2002]) as well as 20 pptv of  $\text{Br}_y$  (nearly a factor of two higher than our estimate of  $\text{Br}_y$  based on published relations with  $\text{N}_2\text{O}$  [e.g., Table 1 of Wennberg *et al.*, 1999]). Even with these assumptions, the measured shape of  $\text{HO}_2$  vs SZA is considerably different than the calculated shape.

The comparisons of measured and modeled  $\text{NO}_2$  and  $\text{NO}$  shown in Figure 10 suggest the actinic flux calculation is carried out correctly [Gao *et al.*, 2001]. For these simulations, the model is perturbed slightly to assure good agreement with measured  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) [Wennberg *et al.*, 1999]. This perturbation is carried out to assure proper model representation of the  $\text{OH}/\text{HO}_2$  ratio. This is particularly important for simulations of  $\text{HO}_x$  due to the auto-catalytic nature of some of the  $\text{HO}_x$  loss processes [e.g., Wennberg *et al.*, 1999].

The final illustration, Figure 11, is identical to Figure 5 of the published paper except the measurements of  $\text{HO}_2$  have been reduced by 30% (the potential systematic error of the  $\text{HO}_x$  observations may be this large [Wennberg *et al.*, 1999]). This figure is included here to support our conclusion that the *Near IR* model reproduces the overall shape of observed  $\text{HO}_2$  throughout the day, whereas the *JPL00* and *Model B* simulations are not in agreement with this measured shape.

## References for Supplemental Material

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**Table 1.** MkIV Measurements of HO<sub>2</sub>NO<sub>2</sub>, Sept. 25, 1993, Sunset.

Altitude	VMR (pptv)	VMR Uncertainty (pptv)
14.	18.48	8.5
15.	15.71	8.1
16.	14.27	8.4
17.	14.81	9.0
18.	18.27	10.
19.	25.52	12.
20.	37.78	13.
21.	56.10	14.
22.	79.94	16.
23.	108.5	18.
24.	138.7	21.
25.	166.0	23.
26.	188.3	26.
27.	203.8	29.
28.	211.0	32.
29.	207.7	34.
30.	195.7	37.
31.	179.5	40.
32.	158.0	43.
33.	132.2	46.
34.	108.7	49.
35.	88.36	53.
36.	68.97	58.
37.	51.13	62.
38.	35.91	69.

**Table 2.** MkIV Measurements of HO<sub>2</sub>NO<sub>2</sub>, May 8, 1997, Sunrise.

Altitude	VMR (pptv)	VMR Uncertainty (pptv)
8.	26.45	32.
9.	34.69	17.
10.	49.62	14.
11.	61.26	16.
12.	59.63	15.
13.	50.25	14.
14.	39.70	14.
15.	34.06	14.
16.	36.99	15.
17.	52.13	17.
18.	78.44	22.
19.	102.5	26.
20.	111.7	28.
21.	116.0	29.
22.	123.6	32.
23.	129.6	34.
24.	132.6	35.
25.	136.3	36.
26.	136.3	38.
27.	122.7	37.
28.	98.53	35.
29.	74.89	34.
30.	57.92	34.
31.	46.64	36.
32.	40.18	39.
33.	35.50	43.
34.	32.14	48.
35.	31.77	58.
36.	35.34	73.
37.	39.25	90.
38.	42.18	110.

**Table 3.** Model Inputs for Sept. 25, 1993, Sunset.<sup>a</sup>

Z (km)	T (K)	p (mbar)	O <sub>3</sub> (ppmv)	H <sub>2</sub> O (ppmv)	CH <sub>4</sub> (ppmv)	NO <sub>y</sub> (ppbv)	Cl <sub>y</sub> (ppbv)	Br <sub>y</sub> (pptv)	CO (ppbv)	Surf. Area ( $\mu\text{m}^2/\text{cm}^3$ )
12.	225.0	210.5	0.037	17.96	1.66	0.368	0.001	0.01	67.7	1.44
14.	211.6	154.1	0.047	7.24	1.72	0.217	0.001	0.01	65.2	1.79
16.	200.0	110.4	0.124	6.08	1.67	0.290	0.100	0.01	43.9	3.64
18.	202.3	78.75	0.437	4.99	1.61	1.09	0.201	3.39	22.6	6.50
20.	209.1	56.57	1.28	4.03	1.48	3.57	0.871	8.34	13.2	5.77
22.	215.6	41.13	2.77	4.62	1.18	8.02	1.929	14.6	11.8	2.88
24.	219.3	30.13	4.50	4.83	1.09	10.2	2.47	15.5	12.7	1.18
26.	222.4	22.16	6.31	4.79	1.09	11.8	2.72	15.7	14.3	0.65
28.	224.5	16.37	7.60	4.88	1.05	14.3	2.94	15.9	16.2	0.45
30.	227.9	12.14	8.27	5.18	0.955	16.7	3.15	16.0	16.0	0.26
32.	230.5	9.047	8.26	5.46	0.876	17.8	3.29	16.0	15.1	0.13
34.	230.4	6.742	8.10	5.45	0.809	18.3	3.31	16.0	16.4	0.066
36.	240.0	5.060	7.97	5.67	0.687	17.6	3.41	16.0	19.0	0.035
38.	242.2	3.826	7.41	5.84	0.660	17.3	3.35	16.0	23.7	0.022

<sup>a</sup> Latitude = 34.5°N; Solar Declination = -1.1°; Albedo = 0.46**Table 4.** Model Inputs for May 8, 1997, Sunrise.<sup>a</sup>

Z (km)	T (K)	p (mbar)	O <sub>3</sub> (ppmv)	H <sub>2</sub> O (ppmv)	CH <sub>4</sub> (ppmv)	NO <sub>y</sub> (ppbv)	Cl <sub>y</sub> (ppbv)	Br <sub>y</sub> (pptv)	CO (ppbv)	Surf. Area ( $\mu\text{m}^2/\text{cm}^3$ )	Lat. (°N)	Albedo
8.	226.9	345.4	0.104	27.80	1.77	0.79	0.005	0.01	89.4	1.54	70.47	0.85
10.	222.5	254.1	0.440	10.10	1.65	2.20	0.447	3.51	37.2	2.45	70.02	0.77
12.	231.1	188.4	0.717	3.02	1.58	3.30	0.718	5.31	20.5	1.52	69.66	0.72
14.	231.0	140.2	0.509	3.09	1.65	1.95	0.356	2.44	27.1	0.957	69.35	0.66
16.	229.3	104.4	0.860	3.51	1.60	2.65	0.662	4.72	18.3	0.944	69.08	0.59
18.	228.2	77.44	2.03	4.59	1.38	6.05	1.58	11.4	12.1	0.900	68.81	0.53
20.	228.8	57.52	2.95	4.82	1.32	8.46	2.10	13.0	12.2	0.706	68.56	0.46
22.	228.6	42.73	3.73	4.89	1.28	9.76	2.28	13.9	13.3	0.480	68.29	0.40
24.	228.5	31.74	4.02	5.13	1.17	12.50	2.86	15.6	14.7	0.287	68.03	0.35
26.	228.9	23.58	4.20	5.44	0.994	15.10	3.16	16.0	15.2	0.173	67.76	0.31
28.	229.6	17.54	4.48	5.76	0.875	16.70	3.46	16.0	15.9	0.102	67.48	0.28
30.	230.8	13.06	4.86	6.07	0.767	17.20	3.50	16.0	15.7	0.061	67.19	0.25
32.	233.2	9.749	5.29	6.25	0.651	16.00	3.53	16.0	16.5	0.035	66.85	0.18
34.	236.0	7.299	6.05	6.34	0.583	14.80	3.41	16.0	18.4	0.023	66.47	0.11
36.	241.3	5.502	6.43	6.42	0.512	13.30	3.21	16.0	18.8	0.018	65.99	0.11
38.	247.4	4.171	6.61	6.64	0.376	10.80	2.91	16.0	19.8	0.014	64.88	0.08

<sup>a</sup> Solar Declination = 17.2°. Latitude and Albedo specified, as indicated, for each altitude.

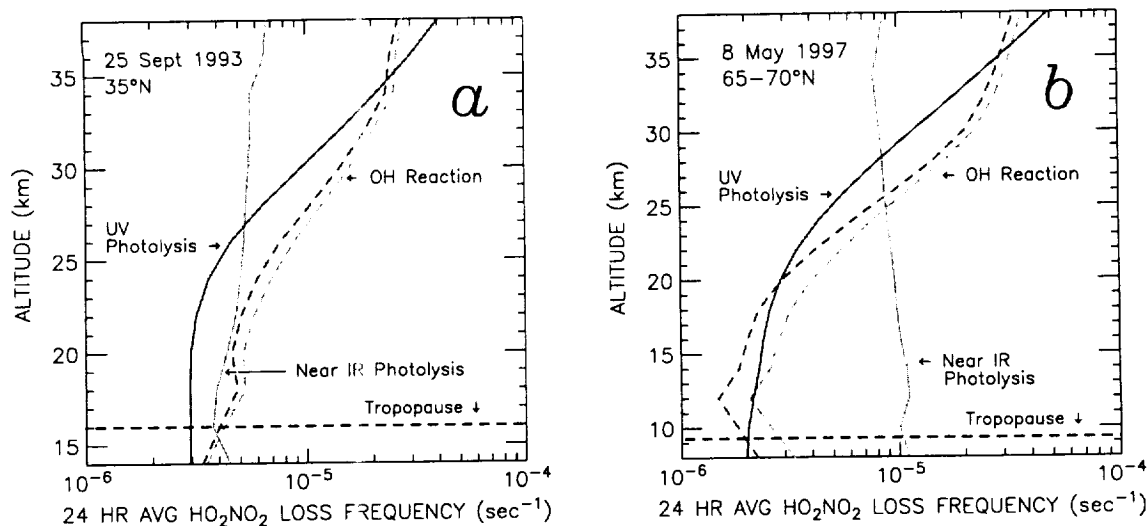


Figure 6. Panel *a*. Calculated loss frequencies of  $\text{HO}_2\text{NO}_2$  for the Sept. 25, 1993 simulation, averaged over 24 hours, due to UV photolysis only using *JPL00* [Sander *et al.*, 2000] cross sections (red solid), due to near IR photolysis only using cross sections of *Roehl et al.* [2002] (green solid), and due to reaction of OH with  $\text{HO}_2\text{NO}_2$  (red dashed for *JPL00* kinetics; green dashed for *Near IR* kinetics). Other sinks of  $\text{HO}_2\text{NO}_2$ , such as thermal decomposition and reaction with atomic Cl, are considered in the model but do not contribute appreciably to the loss of  $\text{HO}_2\text{NO}_2$ . Panel *b*. Same as *a*, for the May 8, 1997 simulation.

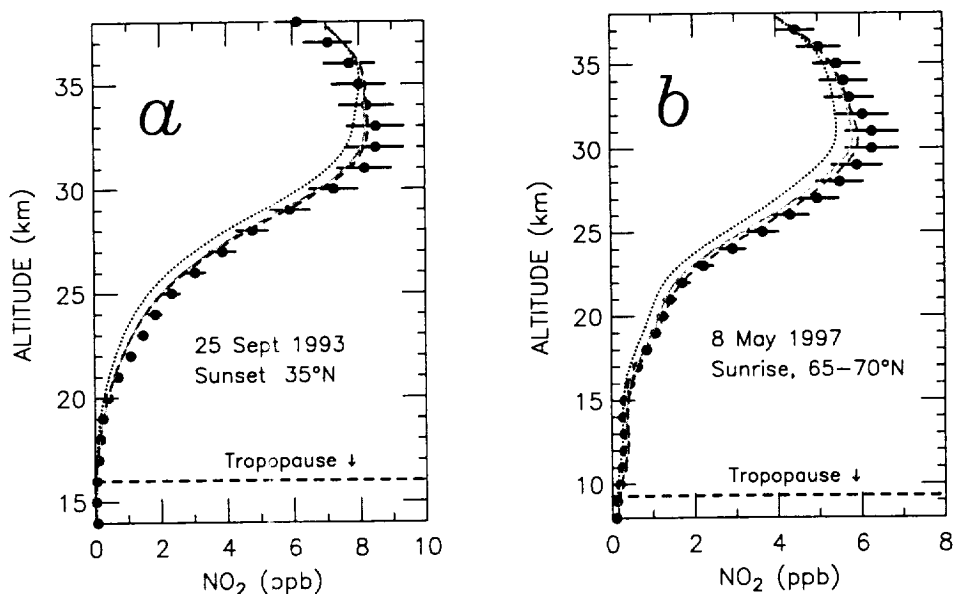


Figure 7. Panel *a*. Profile of  $\text{NO}_2$  measured by MkIV on Sept. 25, 1993 at sunset compared to model simulations for *JPL00* kinetics (red dashed line) and *Near IR* kinetics (green solid line). Also shown, for comparison to earlier published results, is a model result using *JPL97* [DeMore *et al.*, 1997] kinetics (dotted blue line). Results from the *Model B* simulation (not shown) are nearly identical to those from the *JPL00* model run. Error bars on the data denote  $1\sigma$  measurement precision. Panel *b*. Same as *a*, for May 8, 1997 at sunrise.

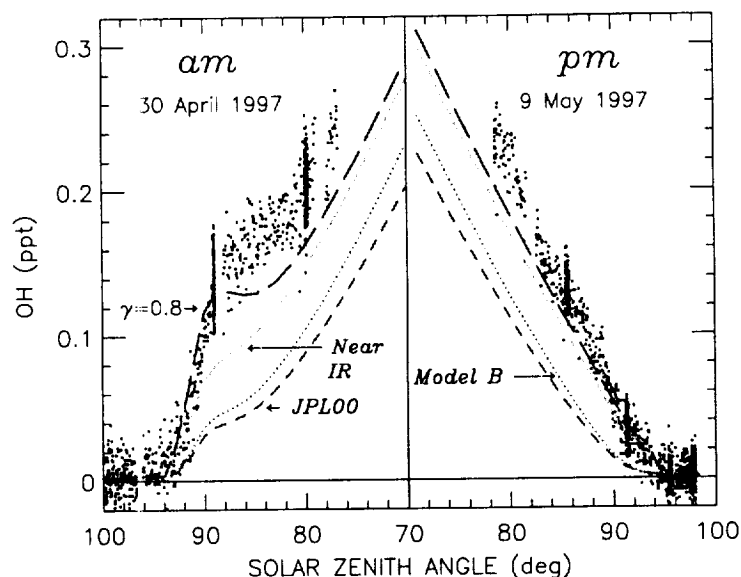


Figure 8. Observations of OH obtained on the morning of April 30, 1997 and the afternoon of May 9, 1997 from the ER-2 aircraft compared to model simulations for four sets of kinetic parameters: 1) *JPL00*; 2) *Model B* (see text); 3) *Near IR* photolysis of  $\text{HO}_2\text{NO}_2$  plus *Model B*; 4) allowing for a reaction probability of 0.8 for  $\text{BrONO}_2$  hydrolysis within the *Near IR* model.

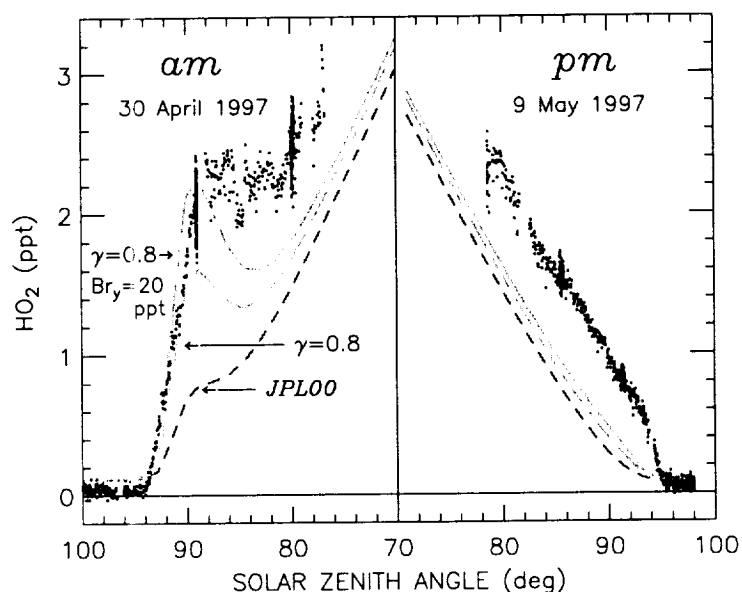


Figure 9. Observations of  $\text{HO}_2$  obtained on the morning of April 30, 1997 and the afternoon of May 9, 1997 from the ER-2 aircraft compared to model simulations for three sets of kinetic parameters: 1) *JPL00*; 2) allowing for a reaction probability of 0.8 for  $\text{BrONO}_2$  hydrolysis within the *JPL00* model; 3) allowing for a reaction probability of 0.8 for  $\text{BrONO}_2$  hydrolysis within the *JPL00* model plus raising the level of  $\text{Br}_y$  from 12.9 pptv [Wennberg *et al.*, 1999] to 20 pptv.

Figure 11. Same as Figure 5 of our paper, except the observations of  $\text{HO}_2$  have been lowered by 30%, which corresponds to the potential systematic error that could be present in the observations.

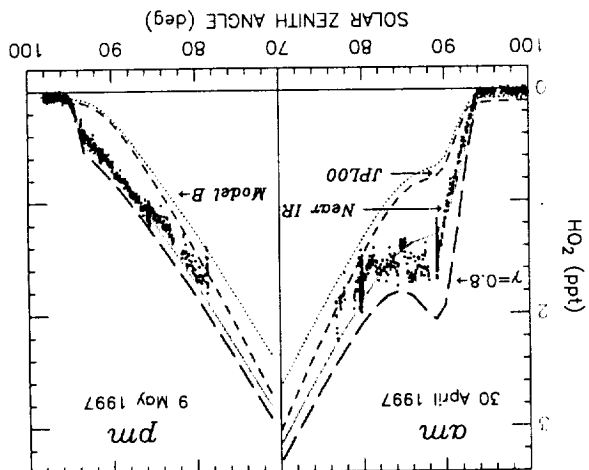


Figure 10. Observations of  $\text{NO}_2$  and  $\text{NO}$  obtained on the morning of April 30, 1997 and the afternoon of May 9, 1997 from the ER-2 aircraft compared to model simulations for *JPL00* kinetics (red dashed line) and *Near IR* kinetics (green solid line). Results from the other simulations (not shown) are nearly identical to those shown. The data are described by Gao *et al.* [2001] and references therein.

